

New Method for Hydroxylating Long-Chain Unsaturated Fatty Acids, Esters, Alcohols, and Hydrocarbons¹

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THE only present commercial source of monohydroxystearic acid is castor oil, a non-domestic oil, from which it is prepared by hydrogenation and hydrolysis. Although figures for the annual production of monohydroxystearic acid are not available, estimates considered to be reliable suggest a range of about three million to five million pounds. Because of the relatively high price and ever-increasing demands for castor oil in the preparation of surface coatings (dehydrated castor oil), lubricating greases (monohydroxystearic acid), lubricants, plasticizers and plastics (sebacic acid), substitutes for castor oil or castor oil products, derivable from readily available, inexpensive domestic materials, have been sought for some time, generally without success.

Inedible animal fats are plentiful and inexpensive agricultural raw materials, and for the past few years a large and growing surplus of these fats has existed. As part of a broad and basic program of research this laboratory has been investigating the expanded utilization of inedible animal fats as sources of industrial chemicals. One object of these investigations has been the efficient preparation of monohydroxystearic acid from oleic acid by relatively simple chemical reactions.

Monohydroxystearic Acids from Oleic Acid

Oleic acid is a readily available and inexpensive material (10-15¢ per pound), and the commercial grades are derived almost entirely from domestic inedible animal fats, of which it is the most important single component. Monohydroxystearic acid has been prepared from oleic acid by addition of sulfuric acid to the double bond followed by hydrolysis, and also by epoxidation to form *cis*-9,10-epoxystearic acid followed by hydrogenation.³

The sulfation of oleic acid involves the handling and dilution of large quantities of concentrated sulfuric acid. This, of course, is well worked out on a large scale, but the hydrolysis of the intermediate sulfate esters and other esters which are resistant to hydrolysis has been a major drawback to the commercial exploitation of the sulfation reaction. Furthermore the resulting monohydroxystearic acids are a complicated mixture of isomers and the melting point of a once-crystallized product is low (57-62°) (6, 8).

The commercial unavailability of *cis*-9,10-epoxystearic acid has been a deterrent to the use of this compound for the preparation of monohydroxystearic acids. It is questionable perhaps whether a two-step synthetic technique, involving the epoxidation of oleic acid as the first step, could compete with monohydroxystearic acid from castor oil. This synthesis cannot be entirely eliminated from consideration how-

ever because the reactions are clean, they give high yields of product, and presumably only two isomeric monohydroxystearic acids are obtained from the oxirane, with the 10-isomer predominating (5, 7).

On the other hand, we have discovered that 90-100% formic acid adds rapidly to the double bond of olefinic compounds at atmospheric pressure yielding formate esters which can be hydrolyzed, if desired, to the corresponding hydroxy compounds in excellent yield (4). This paper describes the catalyzed and uncatalyzed addition of formic acid to some long-chain olefinic compounds derivable from fats and, in particular, the preparation of monohydroxystearic acid from oleic acid. Some comparative experiments are also included in which acetic acid is substituted for formic acid.

When oleic acid (iodine number 89, acid and saponification number, 199) is refluxed with anhydrous formic acid for 24 to 48 hours at atmospheric pressure, the non-volatile residue is a pale-yellow liquid with an iodine number of about 15, a saponification number of about 295, and an acid number of about 170. Furthermore hydrolysis of this residue yields a hard, pale-yellow solid, melting point about 70°, iodine number about 18, percentage of hydroxyl oxygen about 4.1, and saponification and acid number 180-185. It is evident from these results that formic acid has added to the double bond of oleic acid, the original residue is largely formoxystearic acids, and the hydrolyzed product is monohydroxystearic acids.

The addition of anhydrous formic acid to oleic acid is a homogeneous reaction, the excess formic acid is readily recovered by distillation, hydrolysis of the intermediate formoxystearic acids is not time-consuming, and the melting point of the crude monohydroxystearic acids is relatively high and sharp (above 70°), suggesting that the 9- and 10-isomers predominate. Confirmation of this conclusion is shown by the fact that pure 10-hydroxystearic acid, melting point 81°, can be readily isolated in good yield from the mixed monohydroxystearic acids. Furthermore, by using small quantities of perchloric or sulfuric acid or boron fluoride-acetic acid complex (1:2) as catalyst, reaction times of only five minutes with the first and 15 minutes with the last two are required instead of 24 hours when no catalyst is employed.

Table I summarizes the results obtained in the addition of anhydrous formic acid to pure oleic acid. The table shows that a) at room temperature (Expt. 1) or 70° (Expt. 2) addition to the double bond proceeds at an extremely slow rate, but at the reflux temperature (about 105°) of the reaction mixture (Expts. 3, 4, 5) addition takes place at a practical rate; b) the addition of small amounts of perchloric acid as catalyst reduces the reaction time to five minutes or less (Expts. 6, 9, 10, 11), and an increase in reaction time does not result in further addition (Expts. 7, 8; c) sulfuric acid (Expt. 13) and boron fluoride-acetic acid complex (Expt. 15) are also effi-

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³ Other methods of preparation have been reported in the literature, but they appear to have little practical value at the present time.

TABLE I
Addition of Anhydrous Formic Acid to Pure Oleic Acid^a

Expt. No.	Catalyst	Reaction Conditions	Crude Formoxystearic Acids			Crude Monohydroxystearic Acids					Once Crystallized Monohydroxystearic acids ^b			
			I. No.	Acid No.	Sapon. No.	I. No.	Acid No.	Sapon. No.	Hydroxyl Oxygen	M.P. °C.	Acid No.	Hydroxyl Oxygen	M.P.	Yield ^c %
1	None	25°, 168 hrs.	87.3	198
2	None	70°, 24 hrs.	74.0	198	1.09
3	None	Reflux, 8 hrs.	35.4	186	3.17
4	None	Reflux, 24 hrs.	17.0	301	17.7	187	186	4.21	70-72	76-77	70*
5	None	Reflux, 48 hrs.	15.6	171	294	17.9	182	185	4.06	70-71	182	5.2	74-75	70
6	0.5 ml. 70% HClO ₄	Reflux, 0 hrs. ^d	21.0	178	295
7	0.5 ml. 70% HClO ₄	Reflux, ½-4 hrs.	15-16	18.0	176	183	4.09
8	0.5 ml. 70% HClO ₄	Reflux, 24 hrs.	19.2	20.3	172	184	4.00	58-60	187	5.3	66-67	55
9	0.5 or 1 ml. 70% HClO ₄	Reflux, 5-15 mins.	13.5	174	301	15.5	186	189	4.16	73-74	187	5.2	73-74	70*
10	2 ml. 70% HClO ₄	Reflux, 5 mins.	13.8	171	301	15.4	182	184	4.09	72-76	187	5.2	73-74	70
11 ^e	1 ml. 70% HClO ₄	Reflux 5 or 30 mins.	19.3	168	292
12	5 ml. 85% H ₂ SO ₄	Reflux, 5 mins.	78.5
13	5 ml. 85% H ₂ SO ₄	Reflux, 15 mins.	16.1	18.0	183	189	4.20	187	5.4	74-77	60*
14	5 ml. 85% H ₂ SO ₄	Reflux, 8 hrs.	24.2	164	229	25.4	183	186	3.49
15	5 ml. BF ₃ -Acetic Acid Complex (1:2)	Reflux, 15 mins.	16.6	175	76-78	60
16 ^e	5 ml. 100% H ₂ SO ₄	Reflux, 1-4 hrs.	5.4	74.5-76.2	65

^aThe reactants were 100 g. of oleic acid (iodine number 88; composition: 97 + % oleic acid, 2% saturated acids, <0.2% polyunsaturated acids), and 200 ml. of 99-100% formic acid, except Expt. 11 and 16.

^bCalculated for monohydroxystearic acid: acid number, 187; hydroxyl oxygen, 5.33%.

^cThe yield was based on the actual weight of monohydroxystearic acid obtained as a precipitate when the crude monohydroxystearic acid was crystallized from petroleum naphtha (b.p. 65-70°) at 0 to 20°.

^dThe mixture was brought to reflux and reaction was stopped immediately by pouring the solution into cold water.

^eBest conditions are given in these experiments.

^fThe reactants were 100 g. of oleic acid and 100 ml. of 99-100% formic acid.

^gAnhydrous formic acid was replaced by the 90% commercial grade.

cient catalysts and only slightly less efficient than perchloric acid in terms of speed of reaction and yield; d) addition of formic acid proceeds to a maximum of about 80% (Expts. 4, 7, 9, 10, 13, 15); e) there is no apparent difference between the hydroxy acids obtained from the uncatalyzed (Expt. 4) and catalyzed (Expts. 9, 10, 13, 15) experiments provided that long reaction periods are not employed when the strong acid catalysts are present (Expt. 8); and f) the yield of once-crystallized monohydroxystearic acids can be as high as 70% per pass (Expts. 4, 5, 9, 10).

Anhydrous formic acid is a relatively expensive chemical and apparently not too plentiful. When the excess formic acid used as the reaction medium is recovered by distillation, the formic acid content is only about 90% even though it was anhydrous at the outset. It is well known that the rate of decomposition of formic acid to carbon monoxide and water is high when the initial water content is 3% or less, and this decomposition is accelerated by strong acids (1, 9). On the other hand, when its water content is about 10% the decomposition can be neglected, particularly if relatively short heating periods are employed.

Refluxing 90% formic acid with oleic acid gives substantially no addition to the double bond in the absence of acidic catalysts. With sulfuric acid as catalyst however a one-hour reaction period gives about 70% addition whereas with perchloric acid about 16 hours are required, and with boron fluoride-acetic acid two hours are required for 55% addition. The reaction mixtures are heterogeneous throughout the entire reaction period, a fact which probably ac-

counts for the fact that in large-scale laboratory experiments with 90% formic acid much longer reaction times are required.

Addition of acetic acid to oleic acid is negligible at its boiling point, in the absence of catalysts. With perchloric acid, maximum conversion to monohydroxystearic acids is only about 40% in 15 minutes (or one hour), and the yield of isolated monohydroxystearic acids is 30%. With sulfuric acid instead of perchloric acid, poor yields of monohydroxystearic acids are obtained even though the initial reaction products have iodine numbers below 10. Side reactions, probably polymerization, are occurring. The addition of formic acid to oleic acid however proceeds without deleterious side reactions as shown by the fact that the original oleic acid can be entirely accounted for either as olefinic material or monohydroxystearic acids.

Of interest from the practical standpoint is the fact that the olefinic material in the filtrate fraction (iodine numbers 59-68) from the initial crystallization of the crude monohydroxystearic acids also adds formic acid to the extent of about 75%. A 50% yield of monohydroxystearic acids is obtained from the hydrolysis product, thus bringing the overall yield of purified monohydroxystearic acids from oleic acid to over 85% in two passes. The overall conversion is over 95%, based on reduction in iodine number per pass. It is noteworthy that the unsaturated substances in the filtrate are two-thirds *trans* (11) and one-third *cis* even though the starting material is 100% *cis*.

The low-linoleic commercial grades of oleic acid behave substantially the same as does pure oleic acid with respect to degree of addition of anhydrous for-

mic acid. With 90% formic acid however, addition is only about 65%. Yields of once-crystallized monohydroxystearic acids from the commercial oleic acid are lower than from the pure material, as would be expected, since the commercial product is a mixture of octadecenoic acids, and crystallization would cause isomeric monohydroxystearic acids present in relatively small amounts to remain in the filtrate.

Addition of Formic Acid to Other Unsaturated Fatty Materials

Formic acid adds readily to elaidic acid under conditions identical with those of Experiment 9, Table I. Approximately 75% conversion to monohydroxystearic acids is obtained; crystallization of the hydrolysis product gives a 65% yield of monohydroxystearic acids, melting point 77-8°. Similar results are obtained with methyl oleate and oleyl alcohol, the hydrolyzed products consisting of monohydroxystearic acids and dihydroxyoctadecanes, respectively.

Linoleic acid yields approximately equal portions of monohydroxyoctadecenoic and dihydroxystearic acids. The position of the hydroxyl group(s) has not yet been determined. In the dihydroxystearic acid, the hydroxyl groups are not on adjacent carbon atoms.

1-Hexane yields secondary hexyl formates (55%). The composition of this mixture was determined by mild alkaline hydrolysis and fractional distillation of the resulting hexanols through an efficient column. The distillate consisted of $\frac{2}{3}$ 2-hexanol and $\frac{1}{3}$ 3-hexanol; no 1-hexanol could be detected.

Anhydrous formic acid adds readily to 10-hendecenoic (undecylenic) acid, but saponification and acidification of the intermediate formoxy compounds yields polymers primarily. Direct conversion of the formoxyhendecanoic acids to methyl esters also converts the formoxy groups to hydroxyl groups and permits the isolation of methyl monohydroxyhendecanoates in fair yield (48%).

Triglycerides, such as soybean and olive oils, do not add formic acid to the double bond because of their low solubility in formic acid. The addition of a small amount of a mutual cosolvent however, such as butyl acetate or acetic acid, permits the addition to proceed approximately as would be expected for a mixture consisting mainly of glycerides of oleic and linoleic acids (saturated acids are inert; the behavior of linolenic acid is not known). Reactions catalyzed by sulfuric acid yield extremely dark products whereas perchloric acid-catalyzed products darken only slightly. Acidolysis of the glycerides by formic acid proceeds to the extent of only 15-20% if refluxing is continued for only 15 minutes after homogeneity is achieved. Longer reflux times result in progressively higher degrees of acidolysis.

Castor oil does not add formic acid under any conditions so far investigated. Methyl ricinoleate, which is readily soluble in refluxing anhydrous formic acid without the addition of a mutual cosolvent, does not react either. The failure of these two fatty substances to react can be explained on the basis of the electronic effect of the hydroxyl group close to the double bond (4).

Experimental

Starting Materials. Oleic acid and methyl oleate were prepared from olive oil (3). Oleyl alcohol was prepared from a commercial grade (10). *Trans* un-

saturated components were completely absent in these materials (11). Elaidic acid was prepared from oleic acid by elaidinization with powdered selenium (11). Linoleic acid was prepared from corn oil or safflower seed oil (12). 10-Hendecenoic (undecylenic) acid was isolated from a good commercial grade (2). The triglycerides were bleached and refined commercial grades. 1-Hexene, boiling point 62.8-63.0°/753, n_D^{20} 1.3881, was obtained by efficient fractional distillation of the best commercial grade. The low-linoleic oleic acid was a commercial grade, iodine number 92. Anhydrous formic acid and 70% perchloric acid were Eastman Kodak White Label Grade. The 90% formic acid was the best commercial grade. Boron fluoride-acetic acid complex (1:2) was a commercial grade.

Monohydroxystearic Acids. a) *Addition of Anhydrous Formic Acid to Oleic Acid or Methyl Oleate.* A mixture of 100 g. (0.35 mole) of oleic acid (iodine number, 88), 200 ml. of anhydrous formic acid, and 1 ml. of 70% aqueous perchloric acid (1% of the oleic acid) was refluxed for five to 15 minutes in an atmosphere of nitrogen (Expt. 9, Table I). The mixture became homogeneous between 90 and 100°. The excess formic acid, boiling point 43-49°/100, was recovered by distillation under reduced pressure and the residue (crude formoxystearic acid, 112 g.; iodine number, 13.5; saponification number, 301; acid number, 174) was boiled for 15 minutes with a 100% excess of 6 N sodium hydroxide. The hot soap solution was slowly poured into an excess of 6 N hydrochloric acid with stirring, and the oily upper layer was allowed to solidify. The aqueous layer was discarded, and the solid was remelted and stirred with hot water. The solid product was air-dried; it consisted of crude monohydroxystearic acids, 108 g.; m.p. 73-4°; iodine number, 15.5; acid number, 186; hydroxyl oxygen, 4.2%. Its composition was about 78% monohydroxystearic acids, 17% olefinic material, and 5% saturates originally present plus unaccounted for material. Recrystallization at room temperature from petroleum naphtha, hexane fraction (5 ml. per gram of solute) yielded 76 g. (70%) of colorless monohydroxystearic acids, m. p. 73-4°; iodine number, 2; acid and saponification number, 187; hydroxyl oxygen, 5.2%. Calculated for monohydroxystearic acid: iodine number, 0; acid and saponification number, 187; hydroxyl oxygen, 5.3%. Melting points as high as 80° have been obtained on the once-crystallized products. The filtrate from this crystallization had an iodine number in the range of 59-68. Infrared analyses (11) showed that 65-75% of the olefinic substances in these filtrates had the *trans* configuration.

When commercial low-linoleic oleic acid was used instead of the pure material, the yield of isolated monohydroxystearic acids was about 50% even though the extent of the addition of formic acid to the double bond was about 80%.

When sulfuric acid was the catalyst (Expt. 13, Table I), a 15-minute reflux period was required; five minutes were insufficient (Expt. 12, Table I). The once-crystallized product was yellow. Identical results were obtained with boron fluoride-acetic acid complex (Expt. 15, Table I) except that the once-crystallized product was colorless. Results with methyl oleate were the same as with oleic acid.

b) *Addition of 90% Formic Acid to Oleic Acid.* A reaction consisting of 20 g. of oleic acid (0.071 mole),

40 ml. of 90% formic acid, and 2 g. of 100% sulfuric acid required a one-hour reflux period (reaction mixture heterogeneous) to reduce the iodine number to 27-28 (conversion 69%). Up to four hours of reflux gave no further decrease. Recovery of formic acid and hydrolysis of the reaction product, and recrystallization from petroleum naphtha yielded 14 g. (65%) of monohydroxystearic acids, m.p. 74.5-76.2°; hydroxyl oxygen, 5.4%. With 1% perchloric acid as the catalyst a 16-hour reflux period was required for 60-65% conversion, and with 5% boron fluoride-acetic acid (1:2) approximately two hours were required for 55% conversion.

With commercial low-linoleic oleic acid addition to the double bond was about 65% and the overall yield of isolated monohydroxystearic acids was 50%.

c) *Addition of Anhydrous Formic Acid to Elaidic Acid.* Elaidic acid was treated with anhydrous formic acid as described in the first paragraph of a), giving a 75% conversion and a 65% yield of monohydroxystearic acids, m.p. 77-8°.

d) *Addition of Anhydrous Formic Acid to Filtrates.* Thirty-eight grams of the filtrate, iodine number, 64, obtained in the crystallization of the crude monohydroxystearic acids as described in the first paragraph of a), was refluxed for 15 minutes with 76 ml. of anhydrous formic acid and 0.38 ml. of 70% perchloric acid. The formoxystearic acids obtained had the following characteristics: iodine number, 17; acid number, 166; saponification number, 279. Saponification and acidification yielded 39 g. of crude monohydroxystearic acids, hydroxyl oxygen, 3.9%, from which 18 g. of purified product was isolated by crystallization from petroleum naphtha.

e) *Addition of Acetic Acid to Oleic Acid.* When acetic acid was employed instead of formic acid, in the procedure of the first paragraph of a), and the reflux time was either 15 minutes or one hour, the crude acetoxystearic acids had the following characteristics: iodine number, 44; saponification number, 252; acid number, 174. Hydrolysis yielded crude monohydroxystearic acids, acid number, 179; hydroxyl oxygen, 2.24%. Crystallization gave a 30% yield of monohydroxystearic acids, m.p. 75-6°.

Dihydroxyoctadecanes. Fifteen grams of oleyl alcohol (0.056 mole; iodine number, 94), 30 ml. of anhydrous formic acid, and 0.15 ml. of 70% perchloric acid were refluxed for one hour. The reaction mixture was heterogeneous. It was poured into cold water, and the reaction product was dissolved in ether and washed with water until free of acid. The crude formoxyoctadecyl formate (15 g.) was a pale yellow liquid: iodine number, 23; saponification number, 284 (conversion, 75%). It was dissolved in 450 ml. of 0.2 N alcoholic potassium hydroxide, and the alcohol was boiled off on the steam bath. Hot water was added to precipitate the crude dihydroxyoctadecanes as an oil, which solidified on cooling. The lower aqueous layer was discarded, and the solid was remelted with hot water and allowed to resolidify. The hard solid thus obtained weighed 13.4 g. Crystallization from 67 ml. of petroleum naphtha yielded 9.6 g. (60%) of purified dihydroxyoctadecanes, m.p. 62.5-63.5°, hydroxyl oxygen, 10.6% (calcd. 11.2%).

Monohydroxyhendecanoic Acids. A mixture of 100 g. of 10-hendecenoic acid (0.54 mole; iodine number, 132), 200 ml. of anhydrous formic acid, and 1 ml. of 70% perchloric acid was refluxed for 15 minutes. The

reaction mixture was poured into water, and the upper oily layer was dissolved in ether and washed with water until free of acid. Evaporation of the ether yielded 115 g. of crude formoxyhendecanoic acids (amber liquid): iodine number, 11; acid number, 233; saponification number, 404. This product was saponified and excess ice-cold 6 N hydrochloric acid was added to the cooled soap solution with stirring. A viscous amber liquid, neutralization equivalent, 209, was obtained. It was insoluble in petroleum naphtha, and no compound could be isolated from it by crystallization from methanol or mixtures of methanol and petroleum naphtha down to -70°. The oil was therefore converted to methyl esters and distilled, but less than 20% of distillate, b.p. 162-195°/4-5, was obtained. The bulk of the product was a viscous liquid. This suggested that the original saponification-acidification step was undesirable. In a duplicate experiment therefore the crude formoxyhendecanoic acids (115 g.) were refluxed for 4 hours with 230 ml. of anhydrous methanol, containing 2.3 g. of naphthalene-2-sulfonic acid as catalyst. This step simultaneously esterified the carboxyl group and converted the formoxy groups to hydroxyl groups. The catalyst was neutralized with sodium bicarbonate, and the excess methanol was recovered by distillation. The residue (120 g.) was then distilled from an alembic flask and, after removal of a small amount of forerun (8 g.; b.p. 81-106°/0.3), 52 g. (48% yield) of methyl monohydroxyhendecanoates, b.p. 106-113°/0.3-0.6, saponification number, 258, and hydroxyl oxygen, 7.1%, was obtained. (Calculated: saponification number, 255; hydroxyl oxygen, 7.4%.)

Monohydroxyoctadecenoic and Dihydroxystearic Acids. One hundred grams of linoleic acid (iodine number, 160), 200 ml. of anhydrous formic acid, and 1 ml. of 70% perchloric acid was refluxed for 15 minutes. The reaction mixture was poured into cold water, and the upper layer was dissolved in ether and washed with water until free of acid. The ether was evaporated, the last traces under vacuum, yielding 118 g. of an amber oil as a residue: iodine number, 64; saponification number, 326. (A reaction time of one hour yielded a product with the same analytical characteristics.) Saponification and acidification yielded 108 g. of crude hydroxy acids, iodine number 65, saponification and acid number 174; hydroxyl oxygen, 5.2-5.4%. This product was shaken in a separatory funnel containing 1 l. of petroleum naphtha (hexane fraction) and 1 l. of 80% methanol. From the petroleum naphtha layer a viscous amber liquid, hydroxyl oxygen, 1.0% and iodine number, 108, was obtained. This was discarded. The methanol layer yielded 81 g. of a dark semi-solid, iodine number, 59; acid number, 176; hydroxyl oxygen, 5.3%.

The methanol-soluble fraction was converted to methyl esters by refluxing for 2½ hours with anhydrous methanol (2 ml./g.), containing 1.6 g. of naphthalene-2-sulfonic acid as catalyst. The isolated methyl esters, which weighed 90 g., were distilled from an alembic flask under high vacuum, yielding the following fractions:

Fraction	B.P., °C./mm.	Weight, g.	Iodine No.	Hydroxyl Oxygen, %	Appearance
1	113-132/0.05	9	73	3.3	Yellow liquid
2	133/0.04	15	63	5.6	Yellow liquid
3	154/0.05	7	43	7.0	Semi-solid
4	158/0.05	21	9	9.2	White solid
Residue	27	79	1.9	Black tar

Fraction 2 analyzed as methyl monohydroxyoctadecenoate, mainly, and Fraction 4 as methyl dihydroxystearate. The residue was probably mainly linoleate polymers. An α -glycol analysis on Fraction 4 showed the absence of adjacent hydroxyl groups.

An alternative procedure for the isolation of the dihydroxystearic acid fraction was to crystallize the saponified and acidified reaction product from ether-petroleum naphtha at 0°. In this way 25-30 g. of crude dihydroxystearic acids, m.p. 66-77° and hydroxyl oxygen, 8.4-9.2%, was obtained. Recrystallization from 95% ethanol at -20° yielded 12-15 g. of dihydroxystearic acids, m.p. 77-80°, and iodine number, 12.

Secondary Hexyl Formates. One hundred grams (1.19 moles) of 1-hexene, 200 ml. of anhydrous formic acid, and 1 ml. of 70% perchloric acid were mixed and refluxed for 15 minutes at the highest reflux temperature of the mixture (96°). The catalyst was neutralized with sodium bicarbonate, and the reaction mixture was fractionally distilled. After the recovery of 160 g. of formic acid, b.p. 51-57°/125, 94 g. (55% yield) of mixed hexyl formates, b.p. 87.5-95°/125 and saponification number 394-412, was obtained. Hydrolysis of these esters and fractional distillation of the resulting hexanols through a highly efficient column indicated that the formates consisted of about two-thirds 2-hexyl formate and one-third 3-hexyl formate. No 1-isomer could be identified.

Addition of Anhydrous Formic Acid to Soybean Oil. The relatively low solubility of glycerides in formic acid, compared to the other compounds studied, required that a small amount of mutual cosolvent be used. In the absence of a cosolvent substantially no addition of formic acid to the double bond was noted.

Ten grams of soybean oil, iodine number, 135, and saponification number, 191, 20 ml. of anhydrous formic acid, 0.1 ml. of 70% perchloric acid, and 5 ml. of butyl acetate were refluxed for 15 minutes after homogeneity was attained (total reaction time was usually between two and three hours). The reaction solution was poured into water and the upper layer was dissolved in ether and washed with water until acid-free. Evaporation of the ether yielded 9.5-10 g. of formylated soybean oil, iodine number 60-62, saponification number 295-302, and acid number 35-50.

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Summary

A new method for hydroxylating long-chain unsaturated compounds is described which involves addition of formic acid at its boiling point to the double bond followed by hydrolysis of the intermediate formate esters. The addition reaction proceeds slowly in the absence of catalysts, but strongly acidic substances, such as perchloric acid, sulfuric acid, and boron fluoride-acetic acid complex, speed up the addition tremendously.

Monohydroxystearic acids can be prepared in good yield by addition of 90-100% formic acid to the double bond of oleic or elaidic acids, methyl oleate, or the unreacted olefinic material separated from the hydrolyzed reaction product of oleic acid with formic acid, followed by hydrolysis. Similarly prepared are dihydroxyoctadecanes from oleyl alcohol, monohydroxyoctadecenoic and dihydroxystearic acids from linoleic acid, monohydroxyhendecanoic acids (isolated as methyl esters) from 10-hendecenoic (undecylenic) acid, and secondary hexanols from 1-hexene. Triglycerides are readily formylated if a small amount of mutual cosolvent is employed.

Acetic acid in the presence of acidic catalysts also adds to the double bond at its normal boiling point, but yields are lower than with formic acid.

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